THE PROCESS OF COALESCENCE OF DENSE LIQUID DISPERSIONS

Tomáš Míšek[a] and Vladimír Rod[b]

[a] *Research Institute of Chemical Equipment, 108 09 Prague 10 and*
[b] *Institute of Chemical Process Fundamentals,*
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol

Received April 13th, 1987

Physical and mathematical models have been derived and experimentally confirmed for the formation of the hold-up profile in a dense liquid–liquid dispersion and for the rate of coalescence at the interface. Both processes may be characterized by three parameters which can be verified or determined experimentally and further used for design of an industrial unit.

Liquid extraction is a process taking place in a two-phase liquid mixture. With a few exceptions one of the two liquids is being dispersed in the other during extraction and, on completion of the process, has to be coalesced in order that it may be removed from the system. The process of coalescence of liquid dispersions is therefore an inherent part of the extraction process. In comparison with the studies of mass transfer, its equilibria and kinetics, as well as the studies on droplet splitting, the results of research of coalescence are very modest and often ambiguous. This concerns both parts of this problem, i.e. the process of coalescence between the droplets of the dispersion and coalescence at the interface.

This paper is devoted to coalescence at the interface. The rate of this process is affected by the size of the mixing parts of the column extractors and, particularly, by the size of the settlers in the mixer-settler batteries. This makes, in the majority of cases, coalescence controlling phenomenon for the major part of the volume, mass and price of the extractor, for the volume of the solvent hold-up and significantly affecting also the operating cost of the extractor.

Investigations of droplet coalescence at the interface proceeded in several ways characterized best by the experimental technique used:

Studies of the residence time of individual droplets on the flat and convex interfaces. This is a situation that has been solved also theoretically. Of the many scientists that examined this problem one can put forth Gillespie and Rideal[1], Cocbain and McRoberts[2], Charles[3], Mackay and Mason[4], Chen, Hahn and Slattery[5]. The research has shown the controlling process to be the draining of the film of the continuous phase from the space between the droplet and the interface. The whole situation is hydrodynamically complex; the discharge due to the buoyancy leads to the formation of narrowed rim at the periphery. In addition, the van der Waals forces and the electric double layer play a role. Due to the dominating effect of the complex hydrodynamic situation at the cap of the droplet the coalescence of individual droplets cannot be regarded as a phenomenon similar to the coalescence in a swarm of droplets, i.e. dispersion. Attempts to correlate both phenomena cannot and did not succeed. Moreover, the distribution of the residence time of the droplets at the interface is very flat and statistical significance of experimental results even with a fairly large number of measurements is low.

Substantial progress has been achieved by Jeffreys and Davis[6] who developed the concept of a coalescing wedge. Due to the coalescence the height of the dense dispersion decreases pushing the interface with a horizontal shift of the dispersion away from the feed point. The dispersion thus forms a wedge in the experimental vessel and the evaluation of its dimensions may yield intensity of coalescence and its dependence on the height of the dispersion. Unfortunately, the experiments are limited to relatively thin layers and a more accurate characterisation of the counter-current motion of the droplets and the continuum in the wedge is dubious.

A different approach used in his pioneer work on coalescence Ryon[7]. On his experimental equipment, similar to a mixer-settler, he first derived empirical dependence of the intensity of coalescence on the height of the layer. Here too, however, the hydrodynamic conditions in the layer permit one neither to measure nor characterise mutual velocities of the droplets and the continuum. Ryons's approach, however, has become a relatively reliable method for sizing settlers in cases when the heights of the layers investigated are relatively small.

This fact has been criticised by Barnea and Mizrahi[8] who, on an extensive set of works, presented, from the engineering standpoint, the so far most significant contribution to the theory and practice of settler design for industrial processes. Their experimental equipment is an analogy of Ryan's set-up but the operating height of the dispersion is around 1 meter and permits visual observation of the process as well as the sampling of the dispersion from various positions in the layer. A drawback of this method remains the difficulty to define the system hydrodynamically. Barnea and Mizrahi also described and introduced a very useful method of batch tests and their utilization for modelling of continuous settlers. Neither these authors, however, worked out a mathematical model for the coalescence of the dispersions although they did recognize the need for it.

Very extensively studied the droplet coalescence Hartland[9,10] and coworkers[11-13].

The so far performed studies of droplet coalescence essentially do not permit design of coalescing equipment by other methods than transfer of data from experiment to full size. Insufficient physical as well as mathematical model of this process makes the above empirical design unreliable. Little attention has been devoted to individual components of the bulk process of coalescence, particularly to characteristics of the dispersion and its intrinsic hydrodynamic.

This work is an attempt for a new approach to these problems.

THEORETICAL

Classification of Dispersions

Apart from the trivial characteristics of the dispersion by physical properties of the phases, depending on which of the phases is continuous and which is dispersed (sometimes also w/o, o/w), the dispersions differ according to the magnitude of the hold-up and the magnitude of the relative velocity of the dispersed and the continuous phase. The dependence of the hold-up, i.e. the volume fraction of the dispersed liquid in the dispersion, on the velocity of the vertical motion of the droplets and continuum shows that for the same velocity of the dispersed liquid the hold-up may assume two values: a low one, for the so-called p-dispersion (positive slope), or dilute dispersion, or, alternatively, a high one, for the so-called n-dispersion (negative slope), or the concentrated dispersion. Upon decreasing the flow rate of the continuous phase for n-dispersion, the hold-up increases until it reaches a value for which all droplets begin to confine one another. In contrast to solid particles it does not mean that they are in mutual contact, but, instead, there is a thin film of the continuous phase between them. At this moment the character of the mutual flow of the continuum and the dispersion alters. The particles of the dispersion, which were free up to now and their relative motion was essentially derived from the motion of individual droplets in the continuum, become at this point practically immobile and their relative motion with respect to the continuum is derived from the pressure drop due to the flow of the continuum in the interparticle interstices. Such a dispersion is termed dense dispersion. The point of transition between both states (concentrated dispersions and dense dispersions) is a direct analogy of treshold fluidisation for solid particles (transition between the fluidized and the fixed bed). A significant difference between solid particles and droplets rests in that the hold-up of the continuum between solid particles does not further decrease with decreasing velocity in dense liquid dispersion though it may further decrease, depending on the properties of the dispersion, almost up to zero. If this occurs than the originally spherical droplets gradually deform, planar facets appear until they totally change to a polyaedric shape. It is appropriate to call the dispersion with spherical droplets and continuum in the shape of interspherical channels the dense channel dispersion. The other limiting case of polyaedric droplets and planar layers of continuum in between may be termed the dense lamellar dispersion. Between these two extremes there exists a transition type with lamellas and channels. Which of the two types of the dispersion will in fact steady down depends on the ratio of the pressure P acting on the droplets from outside and the internal pressure in the droplets

$$P_{\mathrm{in}} \sim \sigma_{\mathrm{i}}/d\,. \qquad (1)$$

For $P \ll P_{\mathrm{in}}$ we are dealing with the dense channel dispersion and spherical droplets, and for $P \gg P_{\mathrm{in}}$ we are dealing with the dense lamellar dispersion and polyaedric droplets. Transition between them is characterized exclusively by the ratio of the pressures P and P_{in}.

Pressure Acting on Droplets

Droplets in the dispersion are buoyed with respect to the continuum by the force proportional to their volume, the difference of densities and the gravitational constant. The resulting pressure – the force related to a unit of horizontal cross section of the dispersion – is therefore also a function of the magnitude of the hold-up. If the vertical coordinate is defined as positive and increasing in the direction of the gravitational motion of the droplets (usually upwards) and $\Delta\varrho$ as $(\varrho_c - \varrho_d)$ then for the increase of the buoyancy force with height results

$$\frac{\partial P_b}{\partial l} = \Delta\varrho g X \,. \tag{2}$$

If neither the dispersion nor continuum moved the pressure acting on the droplet from the outside would be P_b. In liquids in motion, however, one has to consider also the pressure drop arising from the relative motion of the droplets and the continuum.

On neglecting eventual horizontal components of the flow as irrelevant, one has to adopt the concept that the dispersion and continuum are vertically in the counter-current motion creating a pressure drop whose magnitude may be assessed for the lamellar type of the dispersion on the basis of the following consideration: The theory of the laminar flow, which takes place in such a dispersion in thin planar layers, derives[15] for the pressure drop P_f and the volume flow rate Q the following relationship

$$Q = -\frac{h^3 z}{12\mu_c}\frac{\partial P_f}{\partial l}\,, \tag{3}$$

where h designates the thickness of the layer, l designates its length in the direction of the flow and z designates the width. The model depicts the dispersion as follows: The volume hold-up, X, equals the area hold-up and hence the hold-up in the horizontal cross section through the dense dispersion is

$$X = n\,\pi d^2 \varkappa^2/4 \,. \tag{4}$$

On neglecting the wall effects the total length of the lamellas in the given cross section, corresponding to the width of the layer, z, equals one half of the circumference of the polyaedric droplets.

Thus

$$z = (n\,\pi d\varkappa)/2 \,. \tag{5}$$

The area of the lamellas in a unit cross section is the liquid hold-up, $1 - X$, and d is taken to be constant along the height of the layer. The thickness of the layers (the area of the lamellas divided by their length) then equals

$$h = \frac{1 - X}{X} \frac{d\varkappa}{2}, \tag{6}$$

where for z we have substituted from Eq. (5).

For the relative velocity of the liquid we obtain by combination of Eqs (3) to (6) the following

$$u_R = \frac{Q}{(1 - X)\, hz} = - \frac{\partial P_f}{\partial l} \frac{(1 - X)^2\, d^2 \varkappa^2}{48 \mu_c X^2}. \tag{7}$$

For the dispersion one has to define the velocity of the phases. Without this information one cannot calculate the pressure drop, nor can one make conclusions about the quantity depending on it. In the real case passess through the given element of the dense dispersion both the continuous and the dispersed liquid, and in such a way that their relative velocity equals the sum of the velocities of both phases

$$u_R = \frac{U_d}{X} + \frac{U_c}{1 - X}. \tag{8}$$

Since under the lamellar flow deviations from the model description, local resistances, etc., occur, one must reckon also with a different proportionality costant, C_f which may be lumped also with the value $\varkappa$, similarly as in the derivation of the Kármán–Kozeny equation. The final result then takes the form

$$u_R = - \frac{\partial P_f}{\partial l} \frac{1}{C_f \mu_c} \left(\frac{1 - X}{X} d \right)^2. \tag{9}$$

Identical relationship may be derived on the basis of the concept of hydraulic diameter of the channels for the dense channel layer as well and the flow within it. The constant C_f may be expected different in both cases.

The Hold-up of Dispersed Liquid and Its Profile along the Height

Increased pressure P changes the shape of the droplets and the character of the flow changes too. The change of the shape of the droplets induces, however, in region of nonspherical droplets additional significant change of the hold-up. The major portion of the continuous liquid hold-up is namely contained within the channels; the amount in the lamellas, in contrast, is negligibly small. The internal pressure is here related not to the curvature of the whole spherical droplet, but instead, to the curvature, r, of the walls of the channels, which adjusts so as to equalize the internal and external pressure

$$P \sim \frac{\sigma_i}{r}\,. \tag{10}$$

If for the area of the channels, and hence for the hold-up of the continuous phase holds, as sketched in Fig. 1, the following proportionality

$$1 - X = \frac{2A_{ch}}{A_d} \sim \frac{r^2}{d^2}\,, \tag{11}$$

then a combination of Eqs (*10*) and (*11*) leads to the following one-parameter correlation for the hold-up

$$1 - X = \left(C_x \frac{\sigma_i}{dP}\right)^2 \quad \text{for} \quad X > X_0\,, \tag{12}$$

where X_0 designates the hold-up in the dense dispersion composed of undeformed droplets ($P < P_{in}$), which does not further vary with the height.

From Eq. (*12*) one can obtain by differentiation in region of variable X expressions for the increment of pressure with the length l

$$\frac{d\partial P}{\sigma_i \partial l} = -\frac{1}{2C_x(1 - X)^{1.5}} \frac{\partial X}{\partial l} \tag{13}$$

and by combination with the earlier obtained expressions for the buoyancy (*2*) and

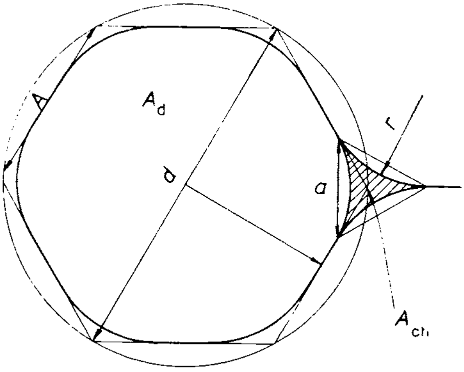

FIG. 1

Derivation of the expression for buoyancy and hold-up in the dense channel dispersion pressure drop (*9*), separation of variables and integration in the limits of the variable hold-up, we obtain

$$d \frac{\int_0^L X(1-X)^{1.5}\,\partial l}{X_0 - X} = a \frac{U_\mathrm{d}}{d} \frac{\int_0^L (X/\sqrt{(1-X)})\,\partial l}{X_0 - X} + b \tag{14}$$

which may be written as a simple linear relationship of the following type

$$y = ax + b\,,$$

where

$$a_0 = \frac{C_\mathrm{f}\mu_\mathrm{c}}{\Delta\varrho g}\,; \quad b_0 = \frac{\sigma_\mathrm{i}}{2C_\mathrm{x}\,\Delta\varrho g} \tag{14a,b}$$

are functions of physical properties of the system and the unknown constants C_f and C_x and

$$y = \frac{d \int_0^L X(1-X)^{1.5}\,\partial l}{X_0 - X}\,; \quad x = \frac{U_\mathrm{d}}{d} \frac{\int_0^L X/\sqrt{(1-X)}\,\partial l}{X_0 - X} \tag{14c,d}$$

are functions of the variables U_d, d, X, and l, which may be found experimentally.

Instead of the integral expression (*14*) one can conveniently use the non-integrated form of the modified Eq. (*13*)

$$\frac{\partial X}{\partial l} = \frac{1}{b_0}\left(dX(1-X)^{1.5} - a_0 \frac{U_\mathrm{d}}{d} \frac{X}{\sqrt{(1-X)}}\right) \tag{15}$$

which may be linearized by introducing

$$y = \frac{\partial X/\partial l}{X/\sqrt{(1-X)}}\,; \quad x = (1-X)^2\,(d^2/U_\mathrm{d}) \tag{16a}$$

in the form

$$y = Ax + B\,, \tag{16b}$$

where

$$A = 1/b_0\,; \quad B = a_0/b_0\,. \tag{16c}$$

Eq. (*15*) is also a suitable starting point for the calculation of the hold-up profile by numerical integration in suitably selected limits.

The Model of Coalescence at the Interface

In accord with the work of Ryon[7] and Barnea[8] increased flow rate of the dispersed phase U_d through a stagnant continuum increases the height of the d-phase and alters its hold-up (the hold-up profile). For the intensity of coalescence the following model has been formulated[16]: The mean residence time of the droplet at the interface is regarded to be directly proportional to viscosity and indirectly proportional to pressure exerted on the droplet

$$\bar{t} = C_c \mu_c / P \,. \tag{17}$$

The proportionality constant C_c is characteristic for the given system. The hold-up of the dispersed phase at the interface of unit area, so-called area hold-up, is described by

$$X_L = n\, \pi d^2 \varkappa^2 / 4 \,. \tag{18}$$

The flow rate through the interface of unit area is then

$$U_d = d X_L P / C_c \mu_c \,. \tag{19}$$

For the calculation of P we shall make use of Eqs (*2*) and (*9*) derived earlier and by arrangement and integration we arrive at

$$P = \int_0^L \partial P = \Delta\varrho g \int_0^L X \partial l - C_f \frac{U_d \mu_c}{d^2} \int_0^L \frac{X}{(1 - X)^2} \partial l \,. \tag{20}$$

Mean values of the hold-up functions are defined in the following manner:

$$\int_{l=0}^L X \partial l = \bar{X} L \,; \quad \int_{l=0}^L \frac{X}{(1 - X)^2} \partial l = \langle X/(1 - X)^2 \rangle\, L \tag{21, 22}$$

and the model of coalescence is arranged into a single linear relationship between the height of the layer and the flow rate

$$U_d / L = a(1 - b U_d) \,, \tag{23}$$

in which

$$a = \frac{d X_L \bar{X}\, \Delta\varrho g}{C_c \mu_c} \,; \quad b = \frac{C_f \mu_c \langle X/(1 - X)^2 \rangle}{\Delta\varrho g d^2 \bar{X}} \,, \tag{24a, b}$$

From the knowledge of physical properties and the hold-up profile one can calculate the constant C_f and the characteristic constant of coalescence C_c.

EXPERIMENTAL

Depending on the purpose the following experiments were carried out:

Vertical profile of the hold-ups. A coalescence apparatus C50, shown schematically in Fig. 2, was used for measurements. The tanks **1** and **2** serve here to store the heavy liquid, this being in our experiments water saturated by corresponding organic liquid. The latter liquid was stored in tanks **3** and **4**. The coalescence apparatus proper **6** consists of coalescence tube 50 mm in diameter where a layer of dense and coalescing dispersion forms from droplets raising from the bottom conical part of the apparatus. The droplets are formed here by slow displacement through a calibrated orifice with sharp edges. Samples of the dispersion may be drawn from the coalescence tube through sampling valves **18** in order to determine its hold-up. The height of the dense dispersion is measured by direct reading on a scale. The amount of the passing organic phase is measured by a rotameter **11**.

The instrument to measure the residence time of individual droplets at the interface **7** has a single discharge nozzle and it is mounted in parallel in the loop to enable comparison of the results. (The results were, in agreement with the statement at the beginning of this paper, incomparable and will not be dealt with in this work.) The materials used were glass, PTFE and stainless steel.

The properties of the liquid systems used in this work are summarized in Table I. The set of results together with the conditions of experiment are given in Table II.

Examples of fitting Eq. (*17*) to experimental results for selected operating conditions and after interpolation are shown in Fig. 3. The agreement with the linear course confirms the tenets of the model. The outlying point in the right hand corner seems to indicate the limits of the region of variable hold-up.

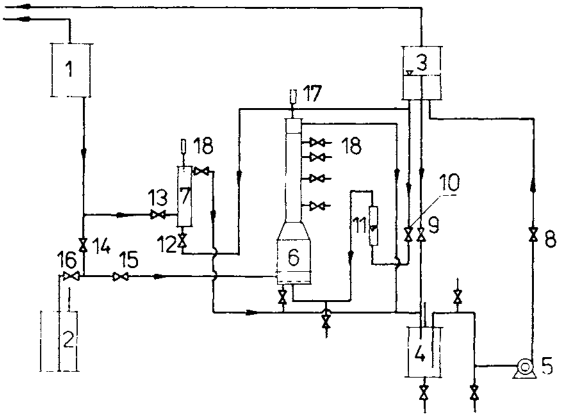

FIG. 2

Scheme of experimental coalescence apparatus C50: **1**—**4** storage tanks, **5** pump, **6** coalescence apparatus, **7** apparatus to measure residence times of droplets at the interface, **8**—**10** valves, **11** rotameter, **12**—**16** valves, **17**, **18** sampling ports

Fitting Eq. (*15*) to experimental data gave relatively good agreement of the experiment with the model for the following values of constants

$$C_f = 31{\cdot}58\,; \quad C_x = 0{\cdot}0071$$

with the standard deviation less than 20%.

The model of coalescence — Eq. (*23*). The same apparatus, C50, was used to measure the dependences of the rate of coalescence U_d on the height of the layer L (refs[16,17]). All systems from Table I were used for measurements. Typical course is shown graphically for one set of conditions in Fig. 4. Good agreement was achieved in all cases. The results clearly confirmed the very good applicability of the model of coalescence according to Eq. (*23*). The evaluation of the constants C_c and C_f, however, did not lead to sufficiently accurate results, as the results are very sensitive to measurements of very low hold-ups of the continuous phase $(1 - X)$, particularly in the vicinity of the interface.

Accordingly, another set of experiments was carried out on an apparatus permitting us to suppress this inaccurracy after the validity of the model had been proven.

The effect of physical properties. The laboratory apparatus developed for further study is shown in Fig. 5. A coalescence tube 1 of diameter 27·5 mm and 0·20 m long was equipped with a glass sieve 5 where droplets of the dispersed (lighter) phase are formed. Its circulation is controlled by a membrane pump 4. The sampling of the condensed dispersion for hold-up measurements is possible through the vent opening. The process takes place with a relatively thin layer of the dense dispersion, satisfying the conditions of constant hold-up. Its magnitude (0·7 to 0·9) substantially enhances the accuracy of the hold-up terms in Eq. (*24*).

TABLE I

Properties of systems used

Properties	System			
	xylene– –water X	1-butanol– –water B	1-butanol– –trichloroethylene– –water BT	1-butanol– –trichloroethylene– –water BTX
Density of water phase (kg/m^3)	998	988	999	995
Density of organic phase (kg/m^3)	858	846	920	915
Difference of densities (kg/m^3)	140	142	79	80
Viscosity of water phase (mPa s)	1	1·23	1·35	1·19
Interfacial tension (mN m)	37·8	1·84	2·72	11·4

TABLE II

Results of experimental hold-up profiles

Height m	Hold-up	Flow rate d-phase m/h	Droplet diameter mm	System
0·04	0·670	0·680	22·8	X
0·22	0·870	0·680	22·8	X
0·51	0·928	0·680	22·8	X
0·04	0·778	0·586	22·8	X
0·18	0·912	0·586	22·8	X
0·04	0·884	1·074	47·5	X
0·62	0·982	1·074	47·5	X
0·25	0·945	1·32	64·6	X
0·28	0·960	1·462	97·0	X
0·04	0·704	0·922	28·2	BT
0·19	0·804	0·922	28·2	BT
0·34	0·884	0·922	28·2	BT
0·04	0·752	1·016	26·0	BT
0·16	0·790	1·016	26·0	BT
0·19	0·901	1·016	26·0	BT
0·03	0·733	0·514	16·8	B
0·09	0·860	0·514	16·8	B
0·15	0·900	0·514	16·8	B

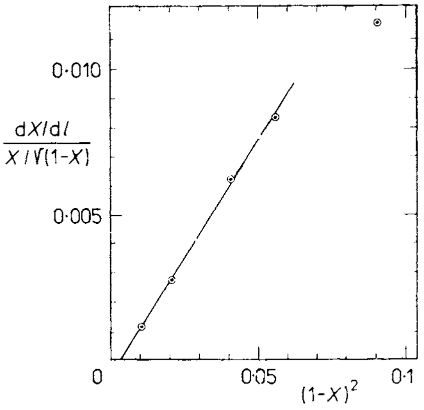

FIG. 3

Graphical illustration of measurement of hold-up profiles according to Eq. (*16*)

An average value of the experimental hold-up 0·8 as a constant was used for evaluation of experiments with this apparatus. The use of individual experimental values of X for individual experiments lead to impaired accuracy of measurements and increased scatter of results. This confirms the plausibility of the assumption of constant hold-up.

A series of experiments was carried out utilizing the Greek-latin square scheme[17]. The components of the organic (dispersed) phase were: toluene, trichlorethylene, methyl isobutyl ketone, the water phase consisted of water and glycerol.

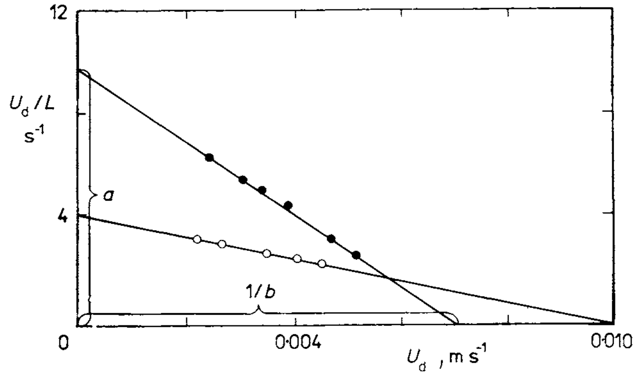

Fig. 4

Graphical illustration of results of coalescence measurements according to Eq. (*23*)

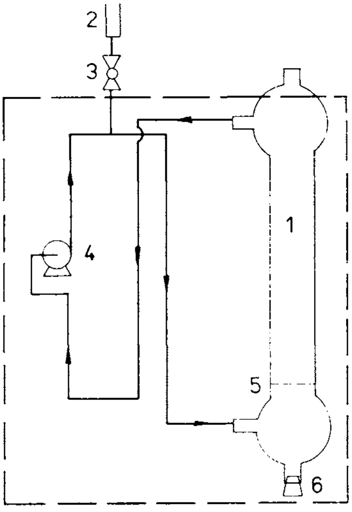

Fig. 5

Scheme of laboratory coalescence instrument C27: 1 coalescence tube, 2 storage tank, 3 transfer valve, 4 membrane pump, 5 glass sieve, 6 discharge plug

The scheme of the square shows Table III together with the average values of physical properties on individual levels. The composition of the phases is shown in Table IV, the results of measurements in Table V.

The average value of C_f was 31·81 carrying an experimental error ±13·8. The coalescence constants C_c ranged between 3 and 32. The evaluated trends suggest the following proportionality

$$C_c \sim \left(\frac{d^2 \varrho_c g}{\sigma_i}\right)\left(\frac{\varrho_c}{\Delta\varrho}\right)^{0.5} . \qquad (25)$$

TABLE III

Experimental conditions according to Greek-latin square for evaluation of the effect of selected physical properties

System No.	μ_c mPa s	$\Delta\varrho$ kg/m^3	σ_i mN/m
11	1·0	130	28·5
12	2·35	130	20·5
13	3·9	130	13·5
21	1·0	70	20·5
22	2·35	70	13·5
23	3·9	70	28·5
31	1·0	30	13·5
32	2·35	30	28·5
33	3·9	30	20·5

TABLE IV

Composition and designation of systems used. Composition given in vol. %

Water phase		Organic phase[a]			Designation
water	glycerol	TOL	TCE	MIBK	
100	0	83·0	4·1	12·9	11
79·0	21·0	57·5	9·0	33·5	12
63·8	36·2	0	25·0	75·0	13
100	0	61·7	12·6	25·7	21
79·7	20·3	0	30·7	69·3	22
65·0	35·0	72·0	28·0	0	23
100	0	0	24·5	75·5	31
78·6	21·4	72·0	28·0	0	32
64·0	36·0	49·0	34·0	17·0	33

[a] TOL toluene, TCE — trichloroethylene, MIBK methyl isobutyl ketone.

The results, however, suffer from a considerable scatter (experimental error 26%) and the correlation is on a low level of statistical significance.

The effect of surfactants. The experimental scheme of the Greek-latin square, according to Table VI, aims at the effect of three surface active agents in various concentrations and after a variable time of contact. Critical concentration of covering the surface, found from measurements of interfacial tension were: Sodium laurylphosphate $C_{cr} = 0{\cdot}0008$ mol/l, alkylbenzenesulphonic acid $C_{cr} = 0{\cdot}0007$ mol/l, alkylpolyglycolether sulphate $C_{cr} = 0{\cdot}00015$ mol/l. The principal system was toluene–water whose properties are given in Table VII. The results of measurements are given in the second half of Table V.

The constant C_f was found 82 on average, the experimental error of individual measurements was 6·3%. The coalescence constant was found 16 on average with an experimental error 12·6%. From the statistical processing one can draw following qualitative conclusions: The dominant effect on the constant of coalescence C_c is that of the degree of covering the surface; fully covered surfaces display markedly decreased intensity of coalescence, which, however, does not further vary by additional surfactants. At the same time the time of contact in the investigated range is statistically insignificant.

TABLE V

Results of measurement of the effect of physical properties and surfactants

System No.	a 1/s	b s/cm	C_c	C_f
		Effect of physical properties		
11	0·54	0·985	5·55	68·26
12	0·32	0·99	3·76	25·95
13	0·0969	1·414	7·21	18·65
21	0·411	1·14	4·05	41·17
22	0·0407	0·960	19·60	18·03
23	0·0584	2·816	9·99	43·11
31	0·0214	1·4	32·05	42·86
32	0·029	2·272	19·27	11·52
33	0·0175	2·415	10·76	10·25
		Effect of surfactants		
11	0·185	1·36	17·12	85·56
12	0·174	1·47	17·97	90·21
13	0·160	1·5	18·32	80·90
21	0·220	1·048	15·25	72·0
22	0·168	1·378	19·60	86·24
23	0·206	1·325	17·24	98·11
31	0·296	1·060	10·82	67·03
32	0·274	1·118	13·63	84·48
33	0·238	0·920	16·35	75·54

The resistance constant C_f reacts sensitively to the type of the surfactant as well as the time of contact. At the coverage of the surface less than 1 it varies insignificantly; fully covered surface, however, decrease its value markedly.

The effect of temperature and contact time. This effect was examined in a simple factorial arrangement where the contact time of freshly purified phases varied between 10 to 56 hours and the temperature between 20 and 50 degrees. The results are summarized in Table VIII.

TABLE VI

Experimental conditions according to Greek-latin square for the evaluation of the effect of surfactants

System No.	Contact time h	Surface coverage %	Agent[a]
11	4	0	A
12	5	0	B
13	6	0	C
21	4	50	B
22	5	50	C
23	6	50	A
31	4	110	C
32	5	110	A
33	6	110	B

[a] A — laurylsulphate sodium, B — alkylbenzenesulphonic acid, C — alkylpolyglycolether sulphate

TABLE VII

Physical properties of systems for the evaluation of the effect of surfactants

System No.	ϱ_c kg/m^3	ϱ_d kg/m^3	$\Delta\varrho$ kg/m^3	μ_c mPa s	σ_i mN/m
11	996	859	137	0·897	35·4
12	996	859	137	0·897	35·3
13	996	859	137	0·897	36·0
21	1 010	859	151	0·962	33·5
22	1 020	859	161	0·970	25·9
23	1 010	859	151	0·925	20·5
31	1 015	859	156	0·965	20·4
32	1 005	859	146	0·913	12·6
33	1 030	859	171	0·967	29·7

The coalescence constants had an average value of 14 and ranged between 8 and 26. The effect of temperature on C_c is directly proportional, small, yet statistically significant. The prevailing effect is that of the contact time which also decreases the intensity of coalescence. This suggests that temperature interacts with the contact time and that both these factors contribute to the retarding accumulation of impurities at the interface. This becomes markedly manifest only at temperatures 40 degress and higher.

The resistance constant increases with the contact time and, on the contrary, decreases with temperature. Its average value amounted to 83 and ranged between 64 and 112.

DISCUSSION

Processing of the primary data pointed clearly at the excellent properties of the model (*15*) and (*23*). Fitting to a linear form is very satisfactory; individual series provide constants C_f and C_c with reproducible values in narrow and expected ranges. A comparison of various series, however, shows differences which may be explained by insufficient accuracy of determination of the hold-up in the dense dispersion. This measurement was carried out by sampling and its accuracy was insatisfactory particularly for the calculation of C_f. The measurement carries probably a systematic

TABLE VIII

The effect of residence time and temperature

Na	a	b	d	$\Delta\varrho$ kg/m^3	μ_c mPa s	σ_i mN/m	C_c	C_f	τ s	t °C
11	0·417	1·089	0·4	131	1	35·7	8·042	89·56	10	20
13	0·29	1·058	0·41	131	1	35·7	11·853	91·42	27	20
15	0·27	1·059	0·43	131	1	35·7	13·35	100·65	35	20
16	0·235	1·053	0·436	131	1	35·7	15·55	102·89	49	20
21	0·479	0·821	0·356	140·5	0·769	35·25	8·69	74·60	10	30
23	0·347	0·8097	0·39	140·5	0·769	35·25	13·14	88·29	27	30
25	0·305	0·7905	0·4	140·5	0·769	35·25	15·33	90·67	35	30
28	0·258	0·769	0·42	140·5	0·769	35·25	19·03	97·25	57	30
32	0·526	0·9803	0·356	145·5	0·632	34·75	9·97	112·23	14	40
34	0·37	0·6535	0·36	145·5	0·632	34·75	14·33	76·51	31	40
37	0·316	0·6172	0·39	145·5	0·632	34·75	18·18	84·80	53	40
38	0·248	0·5865	0·44	145·5	0·632	34·75	26·14	102·57	57	40
42	0·603	0·5376	0·33	150·5	0·538	34·2	9·8	64·26	14	50
44	0·417	0·5494	0·35	150·5	0·538	34·2	15·02	73·88	31	50
46	0·356	0·5586	0·36	150·5	0·538	34·2	18·10	79·47	49	50
47	0·352	0·5465	0·38	150·5	0·538	34·2	19·32	86·62	53	50

error and suffers from large scatter due to random error. For further research it is necessary to develop a method capable of measuring hold-ups of the continuous phase in the range between 0·1 and 30% with an accuracy better than ±10% relative. The method should be contactless – non-interactive.

The results would permit a more accurate formulation of the relationship (*12*), study of the values X and the solution of a number of subsequent questions. A most serious one is the question of droplet coalescence in the layer and corresponding increase of the values d. In the model equation (*23*) one expects constancy of the parameters a and b, which was experimentally confirmed. This in case of high dense layers L means that the undoubted increase of d in the proximity of the interface is in Eq. (*24*) compensated by the decrease of $(1 - X)$ and increase of X, as qualitatively follows from Eq. (*12*). Quantitative solution of this problem is again coupled with a more accurate method of hold-up measurement. These problems nevertheless will not become markedly manifest during measurement or design of settlers with low layers of dense dispersion. Yet, they are vital for the utilization of the method for design of large scale industrial settlers.

The aim of further research, after such a method becomes available, should be a quantitative study of the constants C_c and C_f leading to their physical modelling.

The authors gratefully acknowledge the efficient cooperation of Mr J. Drtina.

LIST OF SYMBOLS

C_c	constant of coalescence
C_f	resistance constant
C_x	hold-up constant
d	diameter of (spherical) droplet, m
g	acceleration due to gravity, m/s^2
h	thickness of film of continuous liquid, m
L	height of layer of dense dispersion, m
l	coordinate of length, m
n	number of droplets in a unit of horizontal cross section of dispersion, 1/m^2
P	pressure exerted on droplet, Pa
Q	volume flow rate, m^3/s
$\bar{t}$	mean residence time of droplet at interface, s
U	velocity of liquid, m/s
u_R	relative velocity, m/s
X	hold-up of dispersed liquid
z	coordinate of length, m
$\varkappa$	shape factor
μ	viscosity, Pa s
ϱ	density, kg/m^3
$\Delta\varrho$	difference of densities, kg/m^3
σ_i	interfacial tension, mN/m
$\langle\ \rangle$	mean value

Subscripts

b	due to buoyancy
c	continuous liquid
d	dispersed liquid
cr	critical value
f	due to friction
in	internal
0	initial value ($l = 0$)
L	end value ($l = L$)

REFERENCES

1. Gillespie T., Riedal E. K.: Trans. Farady Soc. *52*, 173 (1956).
2. Cockbain E. G., McRoberts T. S.: J. Colloid Sci *8*, 440 (1953).
3. Charles G. E., Mason S. G.: J. Colloid Sci. *15*, 105, 236 (1960).
4. Mackay G. D. M., Mason S. G.: Can. J. Chem. Eng. *41*, 203 (1963).
5. Chen J. D., Hahn P. S., Slattery I. C.: AIChE J. *30*, 622 (1984).
6. Jeffreys G. V., Davis G. A. in: *Recent Advances in Liquid-Liquid Extraction* (C. Hanson, Ed.). Pergamon Press, Oxford 1971.
7. Ryon A. D., Daley F. L., Lowrie R. S.: Chem. Eng. Prog. *55*, 70 (1959).
8. Barnea E., Mizrahi J.: Trans. Inst. Chem. Eng. *53*, 61, 70, 75, 83 (1975).
9. Hartland S.: Chem. Eng. Sci. *24*, 987 (1969).
10. Hartland S.: Trans. Inst. Chem. Eng. *45*, 97 (1967).
11. Jeelani S. A. K., Hartland S.: AIChE J. *31*, 711 (1985).
12. Jeelani S. A. K., Hartland S.: Inst. Chem. Eng., Symp. Ser. *94*, Vol. II, 211 (1985).
13. Jeelani S. A. K.: *Thesis*. Eidgenossische Technische Hochschule, Zurich 1985.
14. Míšek T.: Collect. Czech. Chem. Commun. *28*, 1631 (1963).
15. Coulson J. M., Richardson J. F.: *Chemical Engineering*, Vol. I. Pergamon Press, Oxford 1963.
16. Rod V., Míšek T.: *Report* No. 536/64, 604/65. Research Institute of Chemical Equipment, Prague 1965.
17. Němeček V.: *Thesis*. Prague Institute of Chemical Technology, Prague 1968.
18. Kejř V.: *Thesis*. Prague Institute of Chemical Technology, Prague 1967.
19. Heřmanová E.: *Thesis*. Prague Institute of Chemical Technology, Prague 1970.
20. Kloud J.: *Thesis*. Prague Institute of Chemical Technology, Prague 1969.
21. Míšek T.: Collect. Czech. Chem. Commun. *32*, 4018 (1967).

Translated by V. Staněk.